

Non-equilibrium Flow Models and Their Use with General Equations of State

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Abstract

The talk will discuss issues introduced by general equations of state in flow models and solvers for phase separated mixtures in regimes dominated by shock wave interactions where differential shock heating produces large temperatures differences between the components of the mixture. In continuum representations of such flows where interfaces are not explicitly represented, the mixture is described in terms of average quantities such as mass fraction and volume fraction. Such models require closure assumptions to produce a well-posed mathematical model, the most popular of which is pressure-temperature equilibrium between the components at the micro-scale. Such an assumption is not in general going to be a good physical model for time scales that are comparable to the shock wave interactions since the physical processes that could bring the components into thermal equilibrium (such as heat conduction) occur on time scales that are orders of magnitude longer than those of interest for the shock processes. There have been a variety of approaches to multiple temperature flow models. Most of these are based on replacing the thermal equilibrium assumption by a dynamic advection equation [1-2] or by models based on a specific numerical scheme [3], the latter of which are expected to converge to a model of the former type in the limit of an infinitely fine mesh. The published articles usually limited to simple equations of state for the components, such as stiffened gamma law gas or a Mie-Grüneisen type equation of state. We will describe generalizations of these models to mixtures using general equations of state for the components together with methods to handle the complications introduced by such usages.

References

- 1) R. Saurel, O. LeMetayer, A multiphase model for compressible flows with interfaces, shocks, detonation waves and cavitation. J. Fluid. Mech. 431 (2001) 239–271.
- 2) J.W. Grove, Pressure-Velocity Equilibrium Hydrodynamic Models. Acta Mathematica Scientia, 30B(1) (2010) 563–594.
- 3) G.H. Miller, E.G. Puckett, A high-order Godunov method for multiple condensed phases, Journal of Computational Physics, 128 (1996) 134–164.



How the Equation of State Enters into Hydro

- For simplicity we will only discuss inviscid hydrodynamics
- The Euler equations describing the laws of conservation of mass, momentum, and energy for a conservation system:

$$\mathbf{w}_t + \nabla \mathbf{g} \mathbf{F} = \mathbf{S}, \quad \mathbf{w} = \begin{pmatrix} \rho \\ \rho \mathbf{u} \\ \rho \left(\frac{1}{2} u^2 + e \right) \end{pmatrix}, \quad \mathbf{F} = \begin{pmatrix} \rho \mathbf{u} \\ \rho \mathbf{u}^T \mathbf{u} + P \mathbf{I} \\ \rho \left(\frac{1}{2} u^2 + e \right) \mathbf{u} + P \mathbf{u} \end{pmatrix}, \quad \mathbf{S} = \begin{pmatrix} 0 \\ \rho \mathbf{g} \\ \rho \mathbf{u} \mathbf{g} \end{pmatrix}$$

- The equation of state is required to evaluate the flux \mathbf{F}
- Extensions to include material strength, viscosity, thermal conduction, mixtures, mass diffusion, and radiative transport introduce additional constitutive equations that often will require additional equation of state information, in particular the thermodynamic temperature.



Hyperbolic Systems of Conservation Laws and the Ingredients of Flow Solvers

- Partial differential equations in divergence form:

$$\mathbf{u}_t + \nabla \cdot \mathbf{g}(\mathbf{F}) = \mathbf{S}, \quad \mathbf{F} = (\mathbf{F}_1, \mathbf{K}, \mathbf{F}_n)$$

- Hyperbolic: $\mathbf{A}(\mathbf{u}, \mathbf{n}) = \mathbf{n} \cdot \mathbf{g} \frac{d\mathbf{F}}{d\mathbf{u}}$ has all real eigenvalues and a complete set of eigenvectors for every spatial direction \mathbf{n} .

- The integral form of these equations form the basis for virtually all numerical solvers:

$$\frac{d}{dt} \int_{\Omega(t)} \mathbf{u} dV + \int_{\partial\Omega(t)} \mathbf{n} \cdot \mathbf{g}(\mathbf{F}) dA = \int_{\Omega(t)} \mathbf{S} dV, \quad \frac{d}{dt} \int_{\Omega(t)_{\text{fixed}}} \mathbf{u} dV + \int_{\partial\Omega(t)} \mathbf{u} \mathbf{n} \cdot \mathbf{b} + \mathbf{n} \cdot \mathbf{g}(\mathbf{F}) dA = \int_{\Omega(t)} \mathbf{S} dV$$

\mathbf{b} = boundary velocity of the moving body $\Omega(t)$

- Basically all finite volume type solvers seek to time advance the solution by estimating the integral of the flux over the boundary of the region.
- A key technique used in estimating the flux integrals is the characteristic form of the equation which for one spatial dimension can be written as:

$$\mathbf{l}[\mathbf{u}_t + \lambda \mathbf{u}_x] = \mathbf{l} \mathbf{S}, \quad \mathbf{l} \frac{d\mathbf{F}}{d\mathbf{u}} = \lambda \mathbf{l}$$

Characteristics Analysis Deepens the EOS Usage



- A fundamental tool in designing hydrodynamic solvers is the characteristic analysis of the Euler equations
- For simplicity we restrict our attention to one spatial dimension flows and ignore body forces, for smooth flow the equation becomes

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u \frac{\partial}{\partial x}, \quad \frac{D\rho}{Dt} + \rho \frac{\partial u}{\partial x} = 0, \quad \frac{Du}{Dt} + \frac{1}{\rho} \frac{\partial P}{\partial x} = 0, \quad \frac{DS}{Dt} = \frac{De}{Dt} + P \frac{\partial u}{\partial x} = 0$$

- This form introduces the specific entropy S into the flow equations, which is an equation of state function of say the specific internal energy and density
- One can rewrite the above equation in characteristic form by introducing the sound speed c :

$$\left[\frac{\partial P}{\partial t} + (u \pm c) \frac{\partial P}{\partial x} \right] \pm \rho c \left[\frac{\partial u}{\partial t} + (u \pm c) \frac{\partial u}{\partial x} \right] = 0, \quad \frac{\partial S}{\partial t} + u \frac{\partial S}{\partial x} = 0, \quad c^2 = \left. \frac{\partial P}{\partial \rho} \right|_s$$

The Equation of State is Where the Rubber Meets the Road



■ The connection of the hydrodynamic equations with real materials is via the EOS

- The abstract conservation laws of mass, momentum, and energy are completely generic and apply to any flow
- To reproduce the behavior of a real flow requires specifying the relation between the material stress, internal energy, and material deformation
- For hydrodynamics this reduces to specifying the relation between the specific internal energy, mass density, and pressure.

- Typically this is done by giving the pressure as a function of density and specific internal energy:

$$P = P(\rho, e)$$

- This relation is called an incomplete equation of state and is often sufficient for many applications
- More generally, the thermodynamics are related via a potential with the temperature, such as a Helmholtz free energy as a function of specific volume and temperature

$$F = F(V, T), \quad \rho = 1/V, \quad dF = -SdT - PdV, \quad e = F + TS$$

How does one implement a “Real EOS” into a code?

- All aspects of a generic hydrodynamic solver can be written in terms of quantities that are can be described for general equations of state
- In terms of general thermodynamics, the equation of state is defined by a free energy and its derivatives

- Specific Helmholtz free energy: $F(V, T)$, $dF = -PdV - SdT$
- Specific internal energy: $E(V, S)$, $dE = -PdV + TdS$
- Specific Enthalpy: $H(P, S)$, $dH = VdP + TdS$
- Specific Gibb's free energy: $G(P, T)$, $dG = VdP - SdT$
- The free energies are related by Legendre transforms

$$E(V, S) = \sup_T [F(V, T) + TS], \quad F(V, T) = \inf_S [E(V, S) - TS]$$

$$G(P, T) = \inf_V [F(V, T) + PV], \quad F(V, T) = \sup_P [G(P, T) - PV]$$

$$H(P, S) = \inf_V [E(V, S) + PV], \quad E(V, S) = \sup_P [H(P, S) - PV]$$

$$H(P, S) = \sup_T [G(P, T) - TS], \quad G(P, T) = \inf_S [H(P, S) + TS]$$

$$G(P, T) = \inf_{V, S} [E(V, S) - TS + PV], \quad E(V, S) = \sup_{P, T} [G(P, T) + TS - PV]$$

$$H(P, S) = \inf_V \left[\sup_T [F(V, T) + PV + TS] \right], \quad F(V, T) = \sup_P \left[\inf_S [F(V, S) - PV - TS] \right]$$

Specific Heats

- C_V = specific heat at constant volume: $C_V \equiv T \left. \frac{\partial S}{\partial T} \right|_V = \left. \frac{\partial E}{\partial T} \right|_V = -T \frac{\partial^2 F}{\partial T^2}$
 - Often taken as constant for analytic EOS's
- C_P = specific heat at constant pressure: $C_P \equiv T \left. \frac{\partial S}{\partial T} \right|_P = \left. \frac{\partial H}{\partial T} \right|_P = -T \frac{\partial^2 G}{\partial T^2}$
 - Is a quantity that is experimentally measurable
- Thermodynamic stability requires $C_P \geq C_V \geq 0$ (equivalent to convexity constraints on the free energies)

Compressibilities:

- K_T = isothermal compressibility: $K_T \equiv -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T = \frac{1}{PV} \left. \frac{\partial F}{\partial P} \right|_T = -\frac{1}{V} \frac{\partial^2 G}{\partial P^2} = \frac{1}{\rho c_T^2}$
- ρc_T^2 = isothermal bulk modulus
- c_T = isothermal sound speed
- K_S = isentropic compressibility: $K_S \equiv -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_S = \frac{1}{PV} \left. \frac{\partial E}{\partial P} \right|_T = -\frac{1}{V} \frac{\partial^2 H}{\partial P^2} = \frac{1}{\rho c^2}$
- ρc^2 = isentropic (adiabatic) bulk modulus
- c = isentropic (adiabatic) sound speed
- Thermodynamic stability requires $K_T \geq K_S \geq 0$

How does one implement a “Real EOS” into a code?

- **β = coefficient of thermal expansion:** $\beta \equiv \frac{1}{V} \frac{\partial V}{\partial T} \bigg|_P = \frac{1}{V} \frac{\partial^2 G}{\partial P \partial T}$
- **Γ = Grüneisen exponent:** $\Gamma \equiv -\frac{V}{T} \frac{\partial T}{\partial V} \bigg|_S = -\frac{V}{T} \frac{\partial^2 E}{\partial V \partial S}$
- Thermodynamics does not constrain the sign of either β or Γ but most commonly both are positive
- These quantities are related by the formulas:

$$C_V K_T = C_P K_S$$

$$\beta V = \Gamma C_V K_T$$

$$\frac{C_P}{C_V} = \left(1 + \Gamma^2 \frac{C_P T}{c^2} \right) = \left(1 - \Gamma^2 \frac{C_V T}{c^2} \right)^{-1}$$

EOS Examples

- **Stiff gamma law gas:** $(P + (\Gamma + 1)P_\infty)V = \Gamma e$, $e = C_V T + P_\infty V$
 - Simple analytic EOS is easy to implement
 - Very useful in algorithm development since it can be used to add stiffness to the EOS thus stressing the hydrodynamic solver
 - Also useful to approximate more complicated EOS's in limited domains
 - Domain consists of $V > 0$ and $P > -P_\infty$

- **JWL (Jones-Wilkins-Lee) equation of state:**

$$P = \frac{\omega}{V} e + A \left(1 - \frac{\omega}{R_1 V} \right) e^{-R_1 V} + B \left(1 - \frac{\omega}{R_2 V} \right) e^{-R_2 V}, \quad e - e_r(V) = C_V (T - T_r(V))$$

$$\Gamma = \omega, \quad P_r(V) = A e^{-R_1 V} + B e^{-R_2 V}, \quad e_r(V) = A \frac{e^{-R_1 V}}{R_1} + B \frac{e^{-R_2 V}}{R_2}, \quad e'_r(V) = -P_r(V), \quad T_r(V) = T_0 \left(\frac{V}{V_0} \right)^{-\omega}$$

- Simple exponential reference curve makes implementation relatively easy
- Often used to model detonation products
- Large database of parameter values is available from the LLNL HE reference web site (registration required)

EOS Examples: Steinberg-Mie-Grüneisen Equation of State

- **Grüneisen exponent is linear in specific volume:** $\Gamma = \Gamma_0 \frac{V}{V_0} + b \left(1 - \frac{V}{V_0} \right)$

- **Reference Hugoniot formulation (linear U_s - U_p at constant volume):**

$$U_s = c_0 + S(\xi)U_p, S(\xi) = S_1 + S_2\xi + S_3\xi^2, \xi = \frac{V_0 - V}{V_0}$$

- **Energy and pressure are related by a Hugoniot equation:**

$$e_r(V) = e_0 + \frac{P_r(V) + P_0}{2}(V_0 - V)$$

- **Pressure reference is a rational function of specific volume:**

$$P_r(V) = P_0 + \rho_0 c_0^2 \frac{\xi}{[1 - S(\xi)\xi]^2}, \xi = \frac{V_0 - V}{V_0}$$

- **Defined for compression $V \leq V_0$**

- Extensions to expansion generally use a stiff gamma law form
- This introduces a discontinuity in the EOS at the reference density that can impact the solver.

- **Commonly used to model metals as part of an elastic-plastic constitutive model**

- But is used in many other contexts as well, e.g. unburned high explosives

- **Has a complicated formula for the adiabatic and isothermal sound speeds**

- EOS evaluation much more expensive
- Determining whether an evaluation stays in the EOS domain (positive isothermal bulk modulus) can be difficult

More Sophisticated EOS Models

- **Elements and simple compounds are often modeled using electron structure methods, see for example:**
 - S. Eliezer, A. Ghatak and H. Hora, *Fundamentals of Equations of State*. (World Scientific Publishing Co. Ptc. Ltd., Singapore, 2002)
 - R. B. Bird, W. E. Stewart and E. N. Lightfoot, *Transport Phenomena, Second Edition ed.* (John Wiley and Sons, New York, NY, 2007).
- **Plastics and polymers EOS models are usually phenomenological and use a variety of methods**
- **All of these models try to use the best (or any) experimental data available to calibrate their parameters and may require a numerical integration to compute the appropriate free energy**
 - However material property data may be few and far between
 - Hugoniot data for solids
 - Diamond anvil data for quasi-static responses
 - Dynamic thermal data are difficult to obtain experimentally

Tabular Equations of State

- **Pre-computes equation of state data and saves it in a tabular format**

- Most commonly as pressure and specific internal energy matrices as functions of density and temperature

$$P_{ij} = P(\rho_i, T_j), \quad e_{ij} = e(\rho_i, T_j)$$

- Examples include the Los Alamos SESAME database and the Lawrence Livermore National Laboratory LEOS tool
- Some applications take tables of this type and invert them into pressure-temperature based tables

$$\rho_{kl} = \rho(P_k, T_l), \quad e_{kl} = e(P_k, T_l)$$

- This is convenient when evaluating pressure-temperature equilibrium mixtures since the solution method requires frequent EOS evaluations at pressure-temperature points as part of the root finder

- **Allows for the use of arbitrarily complicated (and realistic) EOS models in a format that hides the specific issues of the EOS model from the hydro code**

- Well almost!!

- **Evaluation at off-table points is traditionally done by interpolation**

- Bilinear is fast, but may not be very accurate
- Rational interpolation methods are generally better for computing off table values but are more expensive
- Both methods are only C^0 in pressure and energy and introduce discontinuities into the derived fields across mesh boundaries

How Does One Treat Mixtures?

- **Many applications require multiple materials**
 - We consider here phase separated mixtures that are distinct at the micro-scale
 - Generally not practical to resolve the interfaces in a non-trivial computation
- **In pure Lagrangian schemes or explicit interface tracking methods the materials never mix in the sense that an interface is always present that separates different materials.**
 - In such applications equations of state are only applied to each material separately
- **Mixed cell treatments (multi-component Eulerian, ALE, etc) require additional assumptions in order to compute the thermodynamic properties of the mixture. Mixture Models Include:**
 - Pressure-Temperature-Velocity equilibrium
 - This is the workhorse for most codes treating mixtures
 - Fully molecularly mixed flows (all components occupy the same volume)
 - Used for miscible fluid mixtures and gases
 - Phase separated components with separate temperatures

Equations of Motion

Assume a single velocity and pressure and conservation of component masses, total momentum, and total energy

$$\frac{\partial \mu_k \rho}{\partial t} + \nabla \bullet (\mu_k \rho \mathbf{u}) = 0$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \bullet (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla P = 0$$

$$\frac{\partial \rho \left(e + \frac{1}{2} u^2 \right)}{\partial t} + \nabla \bullet \rho \mathbf{u} \left(e + \frac{1}{2} u^2 \right) + \nabla \bullet P \mathbf{u} = 0$$

$$\rho = \text{total mass density}, \mu_k = \text{mass fraction of component } k, \sum_{k=1}^N \mu_k = 1$$

\mathbf{u} = flow velocity, P = pressure, e = total specific internal energy
Note that this system is under-determined and requires additional assumptions for its closure.

P-T Equilibrium Microstructure

P-T equilibrium: microstructure of the mixture consists of volumetrically distinct components in local mechanical (equal velocity and pressure) and thermal equilibrium.

- **Material components are separated by interfaces/contact discontinuities across which pressure and the interfacial normal component of velocity are continuous**
- **Surface tension between components in the microstructure is negligible (no capillarity due to the microstructure)**
- **Shear across the microstructure interface is negligible (common velocity)**
- **The simulation time scales are sufficiently long that the components have time to come into thermal equilibrium due to un-modeled processes such as thermal conduction (common temperature)**

P-T Equilibrium

- The pressure and temperature for a P-T equilibrium mixture are computed by solving the simultaneous equations:

$$e = \sum_{k=1}^N \mu_k e_k(P, T), \quad V = \sum_{k=1}^N \mu_k V_k(P, T) \Rightarrow P = P(e, V, \mu_1, \dots, \mu_N), \quad T = T(e, V, \mu_1, \dots, \mu_N)$$

- The pressure evolution and sound speed are given by:

$$\frac{DP}{Dt} + \rho c^2 \nabla \cdot \mathbf{u} = 0, \quad \rho c^2 = K_T^{-1}, \quad K_T = \sum_{k=1}^N \alpha_k K_{T,k}(P, T), \quad \alpha_k(P, T) = \frac{\mu_k V_k(P, T)}{V}$$

$$K_T = \text{isothermal compressibility} = K_T = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$$

- In general one can show that the volume fraction satisfies the equation:

$$\frac{D\alpha_k}{Dt} + \alpha_k \left\{ (\beta_k - \beta) \Gamma T + \rho c^2 (K_T - K_{T,k}) \right\} \nabla \cdot \mathbf{u} = 0$$

$$\beta = \text{coefficient of thermal expansion} = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_P, \quad C_P = \text{specific heat at constant pressure} = T \frac{\partial S}{\partial T} \Big|_P, \quad \Gamma = \text{Grüneisen exponent} = \rho \Gamma = \frac{\partial P}{\partial e} \Big|_V$$

$$C_P = \sum_{k=1}^N \mu_k C_{P,k}, \quad K_T = \sum_{k=1}^N \alpha_k K_{T,k}, \quad \beta = \sum_{k=1}^N \alpha_k \beta_k, \quad \frac{1}{\Gamma} = -\beta T + \frac{K_T C_P}{\beta V}$$

- These formulas are sufficient to implement a P-T equilibrium method into a standard hydro solver
 - The resulting system is hyperbolic in domains where all of the components are physical with a single sound speed
 - Allows for a “good” numerical method

Mixed Cell Models: Beyond P-T Equilibrium

- Pressure temperature equilibrium is not correct for strong shock refractions since the shock heating of the separate components occurs on time scales too fast for thermal equilibrium
- Generally for such models one is given a total specific internal energy and specific volume for the mixture together with the mass fractions for the components
- The assumption of a common velocity and pressure is a major simplification of the model. This assumes that the microstructure consists of “well mixed” regions of pure materials. Since the mechanical conditions for a material interface are continuity of pressure and normal component of velocity this means the interface are sufficiently wide spread in the micro-structure to ensure effect continuity of all components of velocity as well as the pressure
- A desirable (but by no means necessary) assumption for such a model is a single mixture sound speed
- Another assumption is that the separate EOS's for the components still apply
 - We require that our formula not depend on any specific EOS assumptions for the components
- Additivity of energy still holds in terms of unknown volume fractions

$$e = \sum_{k=1}^N \mu_k e_k(P, V_k), \quad \alpha_k V = \mu_k V_k \Rightarrow P = P(e, V, \mu_1, \dots, \mu_N, \alpha_1, \dots, \alpha_N)$$

A Formal Model System

- Motivated by the Drew-Passman formal mixture theory
- Single mixture pressure and velocity
- Separate temperatures
- Species' entropy is advected by the common velocity and modified by interactions via P-V work between materials

- **Generic equations:**

$\alpha_k, \rho_k, e_k, T_k$ = component volume fraction, microdensity,
specific internal energy, and temperature

\mathbf{b} = net body force per unit mass

Q_k = is the heat production in species due to interactions between
species and external sources

q = is the total heat production for the mixture due to interactions
and external sources

$$\frac{\partial \alpha_k \rho_k}{\partial t} + \nabla \cdot (\alpha_k \rho_k \mathbf{u}) = 0$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla P = \rho \mathbf{b}$$

$$\frac{\partial \rho \left(e + \frac{1}{2} u^2 \right)}{\partial t} + \nabla \cdot \rho \mathbf{u} \left(e + \frac{1}{2} u^2 \right) + \nabla \cdot P \mathbf{u} = \rho \mathbf{b} \cdot \mathbf{u} + \rho q$$

$$T_k \frac{DS_k}{Dt} = \frac{De_k}{Dt} + P \frac{DV_k}{Dt} = Q_k$$

- **For simplicity we assume the flow is saturated, and that total mass is conserved.**
- **For simplicity we ignore chemistry so the component masses are advected with the flow.**

Question: What are the mathematical consequences for this class of mixture models:

- We can rewrite the component continuity equations in terms of the volume fractions to obtain:

$$\frac{D\alpha_k}{Dt} + \alpha_k \nabla \cdot \mathbf{u} = \alpha_k \frac{1}{V_k} \frac{DV_k}{Dt}$$

- Applying the equation of state for the separate components this becomes:

$$\frac{D\alpha_k}{Dt} + \alpha_k \nabla \cdot \mathbf{u} = \alpha_k \left[\frac{\Gamma_k T_k}{c_k^2} \frac{DS_k}{Dt} - \frac{1}{\rho_k c_k^2} \frac{DP}{Dt} \right]$$

- The assumption of a single sound speed is equivalent to the assumption that the pressure total derivative satisfies the equation

$$\frac{DP}{Dt} + \rho c^2 \nabla \cdot \mathbf{u} = \rho c^2 \mathcal{S}$$

- The form of the source term has yet to be specified

- Substituting this equation we obtain

$$\frac{D\alpha_k}{Dt} = \alpha_k \frac{\Gamma_k T_k}{c_k^2} \frac{DS_k}{Dt} + \alpha_k \left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2} \right] \frac{DP}{Dt} + \alpha_k \mathcal{S}$$

- Physically this equation means that volume changes are driven by heat production in the components and work by pressure
- We also assume that the total energy evolves via an unspecified source term

$$\frac{De}{Dt} + P \frac{DV}{Dt} = \frac{De}{Dt} + PV \nabla \cdot \mathbf{u} = q$$

Proposed Model

- Applying the assumptions from the previous slide into the Drew-Passman formal model for the evolution of the volume fraction and entropies for the components suggests a model of the form:

$$T_k \frac{DS_k}{Dt} = Q_k = -\frac{c_k^2}{\Gamma_k} \left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2} \right] \left(\frac{1 - \delta_k}{2} \right) \frac{DP}{Dt} + q_k$$

$$\frac{D\alpha_k}{Dt} = \alpha_k \left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2} \right] \left(\frac{1 + \delta_k}{2} \right) \frac{DP}{Dt} + \alpha_k \left(\frac{\Gamma_k}{c_k^2} q_k - \mathcal{S} \right)$$

$$\mathcal{S} = \sum_{k=1}^N \alpha_k \frac{\Gamma_k q_k}{c_k^2}$$

- The unspecified quantities δ_k are functions of the flow state and perhaps other physical quantities not included in the basic flow model
 - They may even be solutions to other dynamical equations
- The heat sources q_k would general come from such processes as thermal conduction, radiative transfer, or other energy modifying processes, for simplicity we will take these as zero for the rest of this talk.

Sound speeds

- Taking the mass average of the volume fraction equations and summing the heat equations gives two formulas for the composite bulk modulus:

$$\rho c^2 \sum_{k=1}^N \frac{\alpha_k}{\Gamma_k} \left(\frac{1 - \delta_k}{2} \right) = \sum_{k=1}^N \frac{\alpha_k}{\Gamma_k} \left(\frac{1 - \delta_k}{2} \right) \rho_k c_k^2$$

$$\frac{1}{\rho c^2} \sum_{k=1}^N \alpha_k \left(\frac{1 + \delta_k}{2} \right) = \sum_{k=1}^N \alpha_k \left(\frac{1 + \delta_k}{2} \right) \frac{1}{\rho_k c_k^2}$$

- These equations then provide a constraint on the possible values of the coupling terms:

$$\left[\sum_{k=1}^N \alpha_k \left(\frac{1 + \delta_k}{2} \right) \right] \left[\sum_{k=1}^N \frac{\alpha_k}{\Gamma_k} \left(\frac{1 - \delta_k}{2} \right) \right] = \left[\sum_{k=1}^N \frac{\alpha_k}{\rho_k c_k^2} \left(\frac{1 + \delta_k}{2} \right) \right] \left[\sum_{k=1}^N \alpha_k \frac{\rho_k c_k^2}{\Gamma_k} \left(\frac{1 - \delta_k}{2} \right) \right]$$

- These equations show that for $-1 < \delta_k < 1$ both the bulk modulus and its reciprocal are convex combinations of the component values.
- The values $\delta_k = \pm 1$ correspond to two popular mixture models that will be described subsequently

Pressure Calculation

- In this class of models one generically needs to compute the pressure as a function of the total specific internal energy, total specific volume, component mass fractions and component volume fractions
- This is equivalent to solving the simultaneous set of equations in terms of the unknown pressure and component specific internal energies:

$$P = P_k \left(V_k = \frac{\alpha_k V}{\mu_k}, e_k \right), \quad k = 1, \dots, N, \quad e = \sum_{k=1}^N \mu_k e_k$$

- Note that since we are given both mass and volume fractions together with the total specific volume the component specific volumes are known
- Newton's method for this system provides the iteration:

$$P^{n+1} = \frac{\sum_{k=1}^N \frac{\alpha_k}{\Gamma_k^n} P_k^n}{\sum_{k=1}^N \frac{\alpha_k}{\Gamma_k^n}}, \quad P_k^n = P_k(V_k, e_k^n), \quad \Gamma_k^n = \Gamma_k(V_k, e_k^n), \quad e_k^{n+1} = e_k^n + V_k \frac{P^{n+1} - P_k^n}{\Gamma_k^n} = e_k^n + V_k \frac{\Gamma_k^n}{\Gamma_k^n} \sum_{j=1}^N \frac{\alpha_j}{\Gamma_j^n} [P_j^n - P_k^n], \quad \frac{1}{\Gamma^n} = \sum_{k=1}^N \frac{\alpha_k}{\Gamma_k^n}$$

- If all of the component equations of state are of Grüneisen form: $P_k = P_{r,k}(V_k) + \frac{\Gamma_k(V_k)}{V_k} (e_k - e_{r,k}(V_k))$

We can solve for the pressure explicitly

$$P = P_r(V, \vec{\alpha}, \vec{\mu}) + \frac{\Gamma(V, \vec{\alpha}, \vec{\mu})}{V} [e - e_r(V, \vec{\alpha}, \vec{\mu})], \quad \frac{1}{\Gamma(V, \vec{\alpha}, \vec{\mu})} = \sum_{k=1}^N \frac{\alpha_k}{\Gamma_k(V_k)}$$

$$P_r(V, \vec{\alpha}, \vec{\mu}) = \Gamma(V, \vec{\alpha}, \vec{\mu}) \sum_{k=1}^N \frac{\alpha_k P_{r,k}(V_k)}{\Gamma_k(V_k)}, \quad e_r(V, \vec{\alpha}, \vec{\mu}) = \sum_{k=1}^N \mu_k e_{r,k}(V_k)$$

Specific Models: Uniform Strain

- The value $\delta_k = -1$ corresponds to a popular flow model called variously uniform strain, or more accurately for hydrodynamics, uniform compression:

$$\frac{D\alpha_k}{Dt} = 0, \quad \frac{\Gamma_k}{c_k^2} T_k \frac{DS_k}{Dt} = - \left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2} \right] \frac{DP}{Dt} = \left[1 - \frac{\rho c^2}{\rho_k c_k^2} \right] \nabla \cdot \mathbf{u}, \quad \rho c^2 = \frac{\sum_{k=1}^N \frac{\alpha_k}{\Gamma_k} \rho_k c_k^2}{\sum_{k=1}^N \frac{\alpha_k}{\Gamma_k}}$$

- This model is equivalent to the assumption that all components experience the same volumetric compression:

$$\frac{1}{V_k} \frac{DV_k}{Dt} = \frac{1}{V} \frac{DV}{Dt} = \nabla \cdot \mathbf{u}$$

- Note that the bulk modulus formula depends on the Grüneisen exponent and is a proper convex combination of the component bulk moduli only if all components have positive Grüneisen exponents
 - Positive Grüneisen exponents are the usual case for most EOS models but thermodynamics does not restrict this quantity to be non-negative
- In this model a compressive wave ($DP/Dt > 0$) repartitions entropy by taking heat from species with bulk moduli greater than the composite bulk modulus and assigning it to species with bulk moduli less than the composite value.
 - Since this model should only be used for mixtures with positive Grüneisen exponents, this means that compressive waves cause more compressible (small bulk modulus) materials to relatively gain heat and less compressible materials to relatively cool.

Specific Models: Thermal Isolation

- The value $\delta_k = 1$ corresponds to another popular flow model that is sometimes called thermal isolation

$$T_k \frac{DS_k}{Dt} = 0, \quad \frac{D\alpha_k}{Dt} = \alpha_k \left[\frac{1}{\rho c^2} - \frac{1}{\rho_k c_k^2} \right] \frac{DP}{Dt} = \alpha_k \left[\frac{\rho c^2}{\rho_k c_k^2} - 1 \right] \nabla \cdot \mathbf{u}, \quad \frac{1}{\rho c^2} = \sum_{k=1}^N \frac{\alpha_k}{\rho_k c_k^2}.$$

- This model assumes that there is no heat transfer between material components so that the component specific entropies advect with the flow
- For this model less compressible materials gain relative volume at the expense of the more compressible species
- Of course, neither uniform strain nor thermal isolation can be completely correct since the differential response of the separate materials to compression waves should result in an interaction between materials that exchanges both heat (via P-V work between materials) and volume (via differential compression)

Specific Models: Pressure-Temperature Equilibrium

- As mentioned previously, P-T equilibrium also falls into this class of models. A bit of algebra can be used to show that for this model we have:

$$\frac{1 + \delta_k}{2} = \left(1 + \Gamma_{eq} \beta_{eq} T_{eq}\right) \frac{\rho_k c_k^2}{\rho_{eq} c_{eq}^2} \frac{\rho c_{eq}^2 (K_{T,eq} - K_{T,k}) + \Gamma_{eq} (\beta_k T_k - \beta_{eq} T_{eq})}{\rho_k c_k^2 (K_{T,eq} - K_{T,k}) + (\Gamma_k \beta_k T_k - \Gamma_{eq} \beta_{eq} T_{eq})}$$

- The equilibrium isothermal compressibilities coefficients of thermal expansion are the volume averages of the component values, while the equilibrium Grüneisen exponent is given by the formula:

$$\frac{1}{\Gamma_{eq}} = -\beta_{eq} T + \frac{K_{T,eq} C_{P,eq}}{\beta_{eq} V}$$

- Here the equilibrium specific heat at constant pressure is the mass average of the component values

Shock Structure

- **None of the three models described previously are strictly speaking correct for strong shock interactions**
 - But this never prevented anyone from trying to use them anyway
- **Since neither uniform strain nor thermal isolation are complete conservation laws they do not intrinsically constrain shock relations**
 - Actually uniform strain can be put in conservation form, but whether this is appropriate for a given flow is a modeling question
- **The basic conservation laws of mass, momentum, and energy still apply however and should be satisfied in any theory for shock behavior**
 1. One These laws imply Continuity of mass fraction across mass
 2. The usual Hugoniot relation for energy, pressure, and specific volume

$$\Delta e + \bar{P}\Delta V = 0$$

- **Note that this equation is underdetermined and not sufficient to specify the behind shock state in terms of the ahead state and a shock strength**

Shock Structure: Uniform Strain

- The uniform strain model can in fact be cast in conservation form:

$$\frac{\partial \rho \alpha_k}{\partial t} + \nabla \cdot (\rho \alpha_k \mathbf{u}) = 0$$

- I won't address how physical this assumption actually is
- However if one uses this conservation law, then the continuity of volume fractions across shocks follows which is sufficient to close the Hugoniot equation
- It would be a desirable feature of this model if the Lax stability condition were satisfied:

$$\rho_0^2 c_0^2 < \frac{P - P_0}{V_0 - V} < \rho^2 c^2, \quad P > P_0$$

- This condition asserts that the characteristic of the same wave family as the shock converge into the shock
- Physically, a failure of this condition would lead to unstable shock waves and numerically would probably cause a lot of issues for a code
 - I haven't been able to prove this myself, but it is likely the case for weak shocks and where it fails would point to a limitation of the uniform strain model

Shock Structure: Thermal Isolation

- Unlike uniform strain there appears to be no natural conservation form for the thermal isolation model
- However note that the Hugoniot equation can be rewritten in terms of averages of the component Hugoniot equations

$$\sum_{k=1}^N \mu_k \left[e_k(P, S_k) - e_{k,0} - \frac{P + P_0}{2} (V_{k,0} - V_k(P, S_k)) \right] = 0$$

- This is an immediate consequence of the fact that total specific internal energy and total specific volume are mass averages of the component values
- This suggests that a possible model for shocks using the thermal isolation model is to assume that each component separately satisfies its individual Hugoniot equation

$$e_k(P, S_k) - e_{k,0} - \frac{P + P_0}{2} (V_{k,0} - V_k(P, S_k)) = 0$$

- A nice property of this “separate” Hugoniot model is that one can show that for mixtures all of whose components have positive fundamental derivatives of gas dynamics (equivalent to pressure being a convex function of specific volume at constant entropy) that the Lax stability condition is satisfied for shocks of all strengths

What can go wrong?

- **Almost everything!!**
- **Simultaneous (especially stiff) equations are always a nuisance**
 - High performance solvers might like to use Newton type methods
 - But for many EOS models (especially tabular) the EOS derivatives are apt to be noisy
 - Robust backup solvers such as bisection will generally be necessary
 - How to do this for two equations and two unknowns can be difficult
 - Some EOS formulations might even be in the form of number of materials plus one equations in the same number of unknowns
 - Example: When using density-temperature forms of the EOS
 - Even when things work code performance may be slower than desired
- **The problem of EOS domain for mixtures is to find the intersection of the domains of all the models in the mixture**
 - Many (all?) codes like to be robust and often do some unexpected things to work around the domain issue

What does validation mean in this context

What are some uses of these models?

- **They can be used directly (examples to follow)**
- **Verification of other models**
 - Some mixture models are often expressed only numerically
 - Many pressure relaxation models fall in this class where no mixture pressures are computed and component values are calculated without regard to any mixture constraints
 - Generally an average pressure is computed for use in the momentum equation
 - Relaxation terms are added to the flow equations to encourage the flow to converge towards a single pressure solution
 - Often such models are expected to converge under mesh refinement to a thermal isolation or uniform strain condition so that comparison of wave propagation speeds with those of these two models can be used as additional verification that the solvers are behaving as expected
- **Other processes such as chemistry or radiation transfer can also be incorporated into this frame work**

Test Problem: Two Material Sod Problem

- Riemann problem with two material components

- Initial Conditions:

- Two material components, both perfect gases
 - Component 1 initially in the interface $0 \leq x \leq 0.5$
 $\gamma_1 = 2.0$, $C_{V,1} = 10^{12}$ ergs/gram/eV
 - Component 2 initially in the interface $0.5 \leq x \leq 1$
 $\gamma_2 = 1.4$, $C_{V,2} = 10^{12}$ ergs/gram/eV
- Isothermal initial conditions with a pressure/density jump across the interface

$$\rho(x,0) = \begin{cases} 10^{-3} \text{ grams/cc} & | \quad 0 \leq x \leq 0.5 \text{ cm} \\ 1.25 \times 10^{-4} \text{ grams/cc} & | \quad 0.5 \leq x \leq 1 \text{ cm} \end{cases}, P(x,0) = \begin{cases} 2.0 \times 10^6 \text{ } \mu\text{bar} & | \quad 0 \leq x \leq 0.5 \text{ cm} \\ 10^5 \text{ } \mu\text{bar} & | \quad 0.5 \leq x \leq 1 \text{ cm} \end{cases}$$

$$u(x,0) = 0 \quad | \quad 0 \leq x \leq 1 \text{ cm}$$

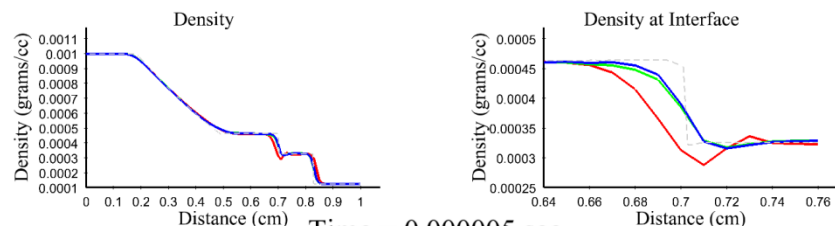
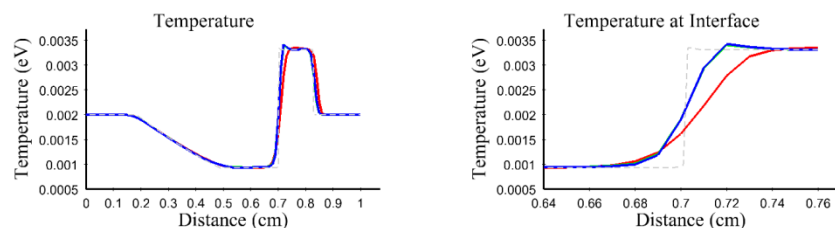
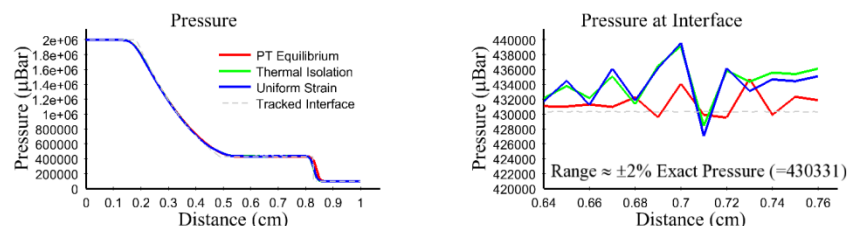
$$e(x,0) = 2.0 \times 10^9 \text{ ergs/gram} \quad | \quad 0 \leq x \leq 1 \text{ cm}, \quad T(x,0) = 2.0 \times 10^{-3} \text{ eV} \quad | \quad 0 \leq x \leq 1 \text{ cm}$$

Test Problem: Two Material Sod Problem

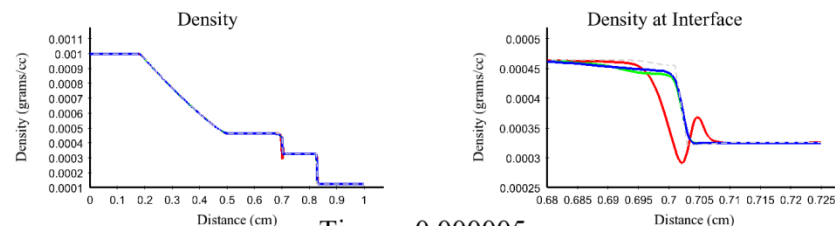
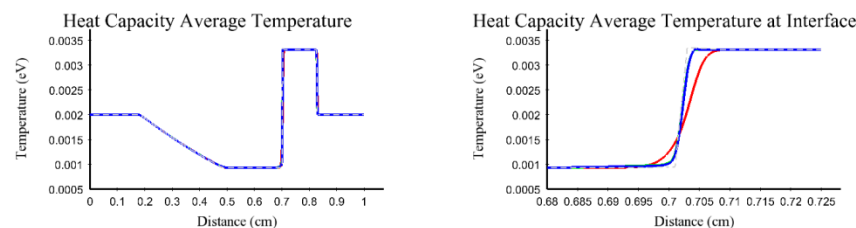
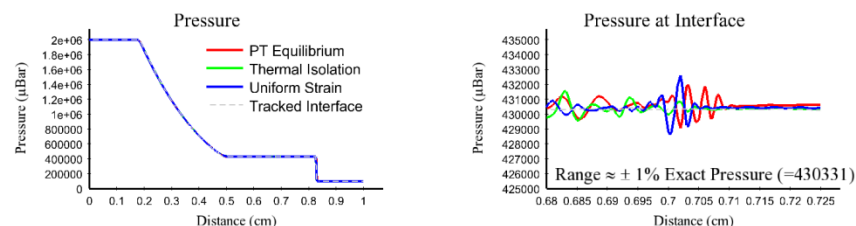
- Main effect to temperature equilibrium is an increase in the width of the transition layer at the interface

- 100 mesh zones

- 1000 mesh zones



Time = 0.000005 sec



Time = 0.000005 sec

- ≈ 100 cycles

- ≈ 1000 cycles

Test Problem: Strong Shock Refraction

■ A Mach 15 shock accelerates the interface between two materials

■ Initial Conditions:

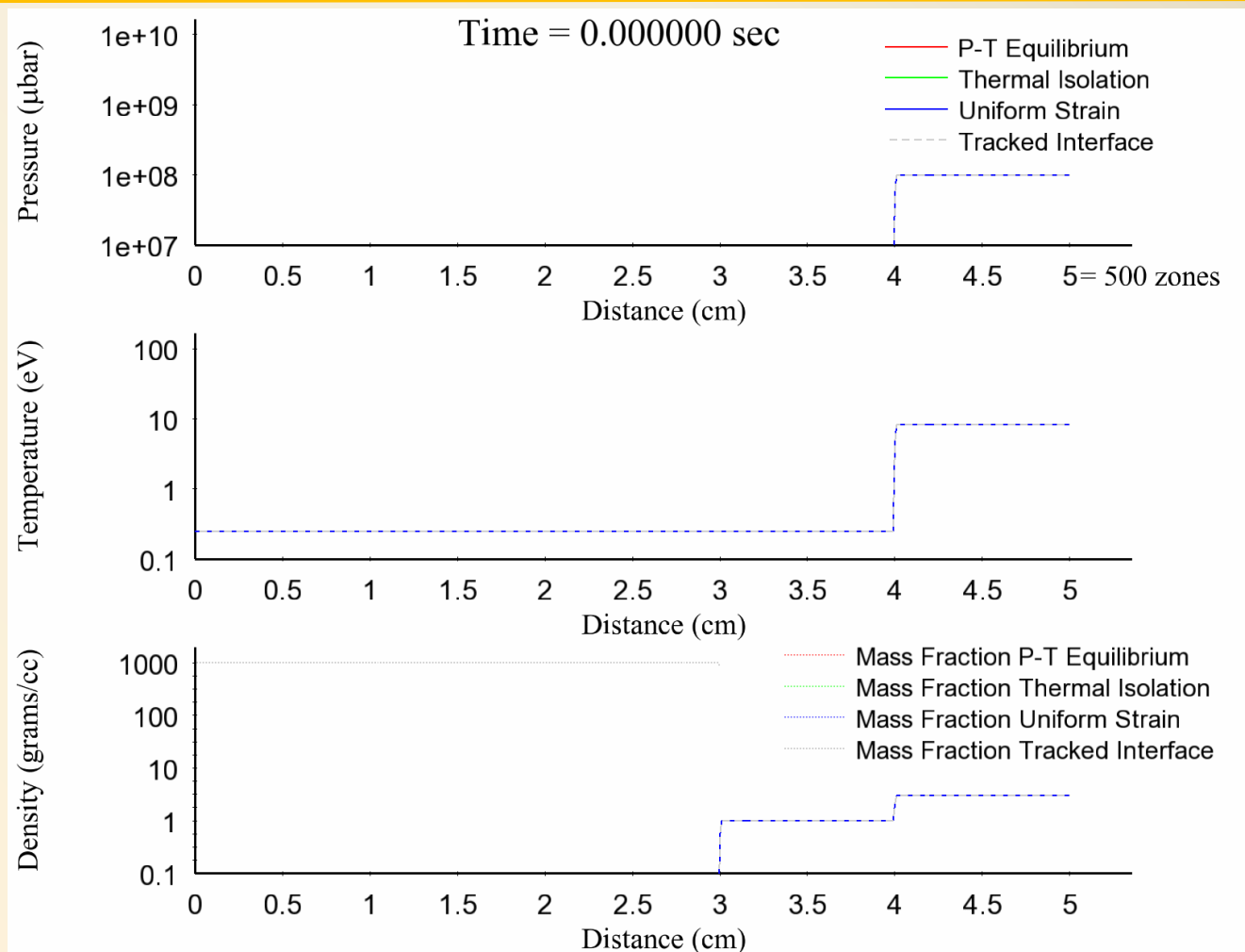
- Spherical Symmetry
- Two material components, both perfect gases
 - Component 1 initially in the interface $0 \leq x \leq 3$ cm
 $\gamma_1 = 1.1$, $C_{V,1} = 4 \times 10^{10}$ ergs/gram/eV
 - Component 2 initially in the interface $3 \leq x \leq 10$ cm
 $\gamma_2 = 2.0$, $C_{V,2} = 4 \times 10^6$ ergs/gram/eV
- Isothermal initial conditions with a density jump across the interface

$$\rho(x,0) = \begin{cases} 10^{-3} \text{ grams/cc} & | \ 0 \leq x \leq 3 \text{ cm} \\ 1.0 \text{ grams/cc} & | \ 3 \leq x \leq 4 \text{ cm} \end{cases}, \quad e(x,0) = \begin{cases} 10^{10} \text{ ergs/gram} & | \ 0 \leq x \leq 3 \text{ cm} \\ 10^6 \text{ ergs/gram} & | \ 3 \leq x \leq 4 \text{ cm} \end{cases}$$

$$P(x,0) = 10^6 \text{ } \mu\text{bar} \quad | \ 0 \leq x \leq 4 \text{ cm}$$

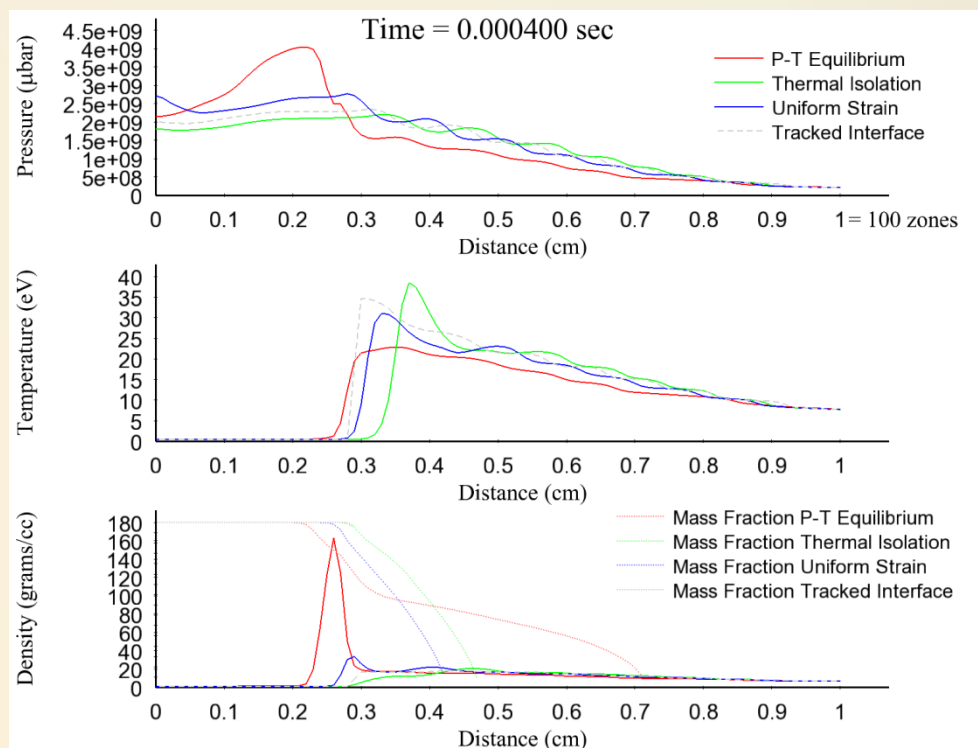
$$u(x,0) = 0 \quad | \ 0 \leq x \leq 4 \text{ cm}, \quad T(x,0) = 0.25 \text{ eV} \quad | \ 0 \leq x \leq 3 \text{ cm}$$
- A density of 3 grams/cc and a pressure of $10^8 \text{ } \mu\text{bar}$ is initialized for the region $4 \leq x \leq 10$ cm, with zero initial velocity

Test Problem: Strong Shock Refraction



Test Problem: Strong Shock Refraction

- P-T equilibrium has fast wave speed and much broader diffusion layer



Conclusions

- Assuming a mixture model satisfies the single velocity/single pressure/single sound speed within a mixed cell leads to a class of models
- Two of the most popular mixture models can be regarded as the extremes of this class of models and are in a sense dual to one another
- One effect of breaking temperature equilibrium is that it allows sharper resolution of shocked material interfaces
- The formulas for the mixture properties discussed here offer additional avenues for code verification for other models
- Implementation of the uniform strain/thermal isolation into existing hydro-codes is possible
- EOS domain and stiffness are major issues that need to be addressed for a practical implementation